Aggregation properties of phosphodiester-linked squaraine oligomers in aqueous solutions

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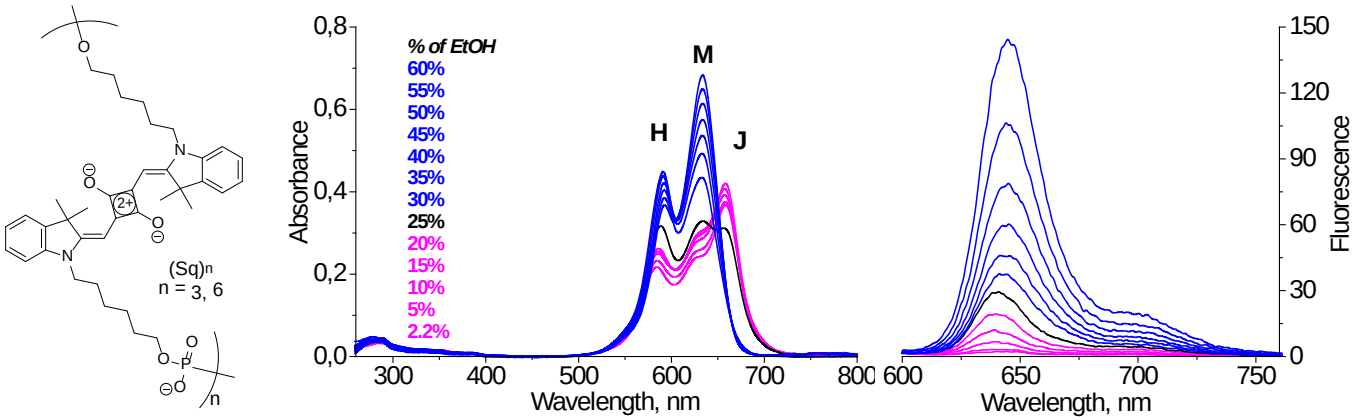
In the search for new compounds for supramolecular chemistry we synthesized the squaraine oligomers $(Sq)_3$ and $(Sq)_6$, and studied their spectral properties in aqueous solutions. The synthesis of the oligomers was performed by a phosphoramidite approach. Absorption and fluorescence spectra of the oligomers were measured in aqueous solutions containing various concentrations of ethanol.



Absorption (left) and fluorescence (right, λ_{ex} = 585 nm) spectra of the oligomer $(Sq)_3$ depending on the concentration of ethanol in the aqueous solution. Conditions: 1 µM of the oligomer, 10 mM phosphate buffer, 100 mM NaCl

Absorption spectra and fluorescence intensities strongly depend on the ethanol content. At concentrations below 20%, the absorption spectrum of $(Sq)_3$ shows the splitting of the main band (632 nm) into a long-wavelength shifted J-band (658 nm) and a short-wavelength shifted H-band (585 nm), which corresponds to an oblique orientation of the transition dipole moments. Ethanol contents above 30% reveal only absorption due to monomer and H-aggregate. The degree of H-aggregation decreases with increasing quantity of ethanol. The absorption spectrum of oligomer $(Sq)_6$ demonstrates a similar response to the change of ethanol percentage. Fluorescence of the oligomers $(Sq)_3$ and $(Sq)_6$ is nearly undetectable at minimal ethanol concentration (2%). Upon increasing the ethanol concentration, the fluorescence intensity grows, which is explained by dissolution of non-emissive aggregates.

Due to their ability to form supramolecular aggregates in aqueous solutions and their absorption properties in the long-wavelength region of the visible spectrum, the amphiphilic squaraine oligomers shown here are promising compounds as components of new materials with diagnostic, biomedical and electronic applications.